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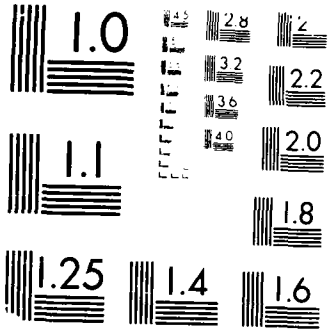

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Work by J. D. Joannopoulos and his collaborators is summarized here.

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J. D. Joannopoulos

22 December 1987

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Research Laboratory of Electronics
Cambridge, Massachusetts 02139

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
DEPARTMENT OF PHYSICS
CAMBRIDGE, MASSACHUSETTS 02139

22 December 1987

Captain Kevin Malloy
AFOSR-NE
Bldg. 210 Rm. 219
Bolling AFB
Washington D.C., 20332-6448

Dear Kevin,

Please consider this my progress report for one year since Nov. 1986. I enclose copies of two publications.

Very briefly our efforts this past year have been directed toward the development of an ab-initio formalism to study grain boundaries in solids.

The microscopic characterization of grain boundaries in polycrystalline semiconductors has become essential to our understanding of the physical properties of these technologically important materials. From a theoretical standpoint, this requires a formal quantum mechanical treatment of the total energy of the grain boundary core region which should properly take into account the redistribution of electron charge density and the unrestricted relaxation of the ions. First principles approaches to calculating the total energy of solids have begun to be applied to grain boundaries in semiconductors and metals. However, the methods employed in these studies have not been entirely ab initio in the sense that assumptions regarding the starting atomic configuration were made or that the potential functions were semi-empirical. Recently, however, we succeeded in performing a completely ab initio investigation of the structure of a grain boundary in geranium. This was accomplished using a quantum molecular dynamics simulated annealing method. This method allows global minimisation of the boundary energy to be achieved with respect to

all electronic and ionic structural degrees of freedom using ab initio local pseudopotentials. The method has significant advantages in computational speed and storage requirements over traditional total energy techniques, especially when systems of low symmetry are involved or in which large relaxations take place.

Various interesting results emerge including identification of two low energy S=5 (001) twist boundary structures, calculation of boundary formation energies, determination of boundary volume changes, and identification of novel intrinsic grain boundary defects such as four-fold rings of bonds and overcoordinated atoms.

At present, we are performing calculations of the valence electron charge density in the neighborhood of the boundary, in order to determine the exact nature of local interatomic bonding. We are also engaged in mapping out the total energy in a dense grid of translation states in order to obtain a global view of the energy surface.

Sincerely,

J. D. Joannopoulos

J. D. Joannopoulos
Professor of Physics

Ab Initio Determination of the Structure of a Grain Boundary by Simulated Quenching

M. C. Payne,[a] P. D. Bristowe, and J. D. Joannopoulos
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
(Received 5 January 1987)

Results of the first completely *ab initio* investigation of the microscopic structure of a grain boundary in a semiconductor are presented. By use of the molecular-dynamics–simulated annealing method for performing total-energy calculations within the local-density–functional and pseudopotential approximations, the $\Sigma=5$ (001) twist boundary in germanium is studied. A number of rotation-and-translation states are investigated leading to a prediction for the structure of this geometry. Evidence for the possible presence of novel defects and glasslike tunneling-mode states at grain boundaries is presented.

PACS numbers: 61.70.Ng, 68.35.Ja, 68.35.Md

Internal interfaces in a solid, such as grain boundaries, often control the mechanical, chemical, and electrical properties of the material. It is essential, therefore, to have an understanding of their structure at an atomic level. Unfortunately, the structural complexity of grain boundaries makes their study a formidable task both experimentally and theoretically. Recently, experimentally, new electron-diffraction and imaging techniques have begun to yield detailed structural information about a number of grain boundaries in special tilt and twist orientations.[1-5] On the theoretical side, first-principles approaches to calculating the total energy of solids have begun to be applied to interfaces.[6-10] These studies have provided important information on the distribution of charge density at the boundary, the local density of states, the atomic structure, and the boundary energy. However, the methods employed so far have not been entirely *ab initio* in the sense that a starting atomic configuration has been assumed based on geometric models or experimental observations.

In this paper we present a completely *ab initio* investigation of the structure of a twist grain boundary in germanium where nothing is known about its microscopic structure. A method is employed which provides for the self-consistent and simultaneous relaxation of the atomic and electronic coordinates. The only input data are the atomic number and mass of germanium.

Specifically, we consider the $\Sigma=5$ (001) twist boundary in the diamond structure, where Σ is the inverse density of coincidence sites. Two distinct $\Sigma=5$ boundary structures with the same coincidence site lattice (CSL) can be formed by rotating one diamond half-crystal with respect to another about the [001] direction by 36.9° or its complementary angle, $-53.1°$.[11] Both structural variants are studied in the present work and are designated $\Sigma5$ and $\Sigma5^*$. As an example, in Fig. 1(a) we illustrate the atomic positions of two layers on either side of an *ideal, unrelaxed* $\Sigma5$ boundary. In this case, the axis of rotation passes through the atom at the center of the indicated unit cell. Experimentally, it is not possible to constrain the position of this axis to any specific translation state and a given rotation state will adopt the translation state of the lowest energy. Since the position of this rotation axis is *a priori* unknown to within a "displacement-shift-complete" vector[12] of $\frac{1}{10}\langle 310\rangle$,[13] it becomes a challenge to theory to predict the appropriate lowest-energy translation state.

It is not possible, however, to calculate the energies of all the translation states within a displacement-shift-complete lattice unit cell. In this work we study the CSL configurations for both rotation states, the $\frac{1}{20}\langle 210\rangle$ translation state of $\Sigma5$ and the $\frac{1}{10}\langle 210\rangle$ translation state of $\Sigma5^*$. These particular states were chosen because the structures have higher symmetry than boundaries produced by arbitrary translation states. Moreover, in the pair-potential simulation[14] of fcc twist boundaries in metals, such states appear to have the lowest energies. Whether this is true for semiconductors is certainly not clear. Nevertheless, for simplicity, we restrict ourselves to these four rotation-and-translation states.

The grain-boundary structures were modeled within the supercell approximation which imposes periodicity *normal* to the interface boundary. Experimentally, it is found that grain-boundary "widths" in semiconductors are extremely narrow ($\lesssim 10$ Å)[5,15] so that a relatively small number of atomic layers on either side of the interface can accurately model the system. Our supercell contains twelve layers of atoms representing two six-layer crystal slabs rotated relative to each other by either 36.9° or $-53.1°$. All the atoms in the supercell were allowed to relax except for the atoms in the central two layers of each crystal slab which were confined to their crystallographic positions. In addition, the distance between these fixed layers was allowed to vary as the local grain-boundary volume changed. The atomic positions and local grain-boundary volume were assumed to have reached their equilibrium values when the forces had become smaller than 0.1 eV/Å.

The calculations were performed with use of the molecular-dynamics simulated quenching method for total-energy calculations.[16,17] The exchange-correlation potential was calculated within local-density-functional theory with use of the Perdew and Zunger parametrization.[18] The electron-ion interaction was determined with

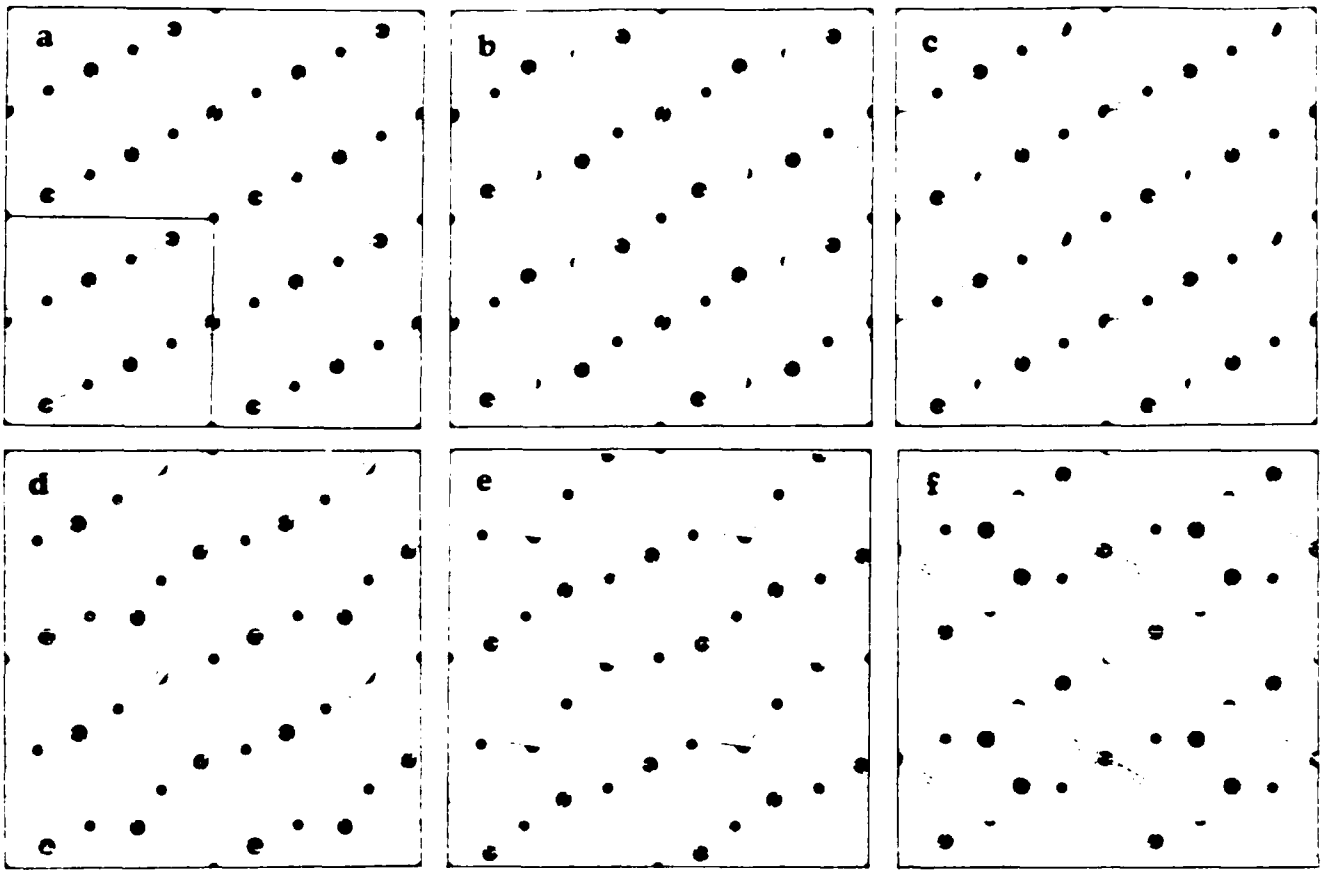

FIG. 1. Atomic positions in planes normal to the (001) direction for two layers above (open circles) and below (filled circles) a twist-grain boundary in germanium. (a) Unrelaxed Σ5 CSL; a typical unit cell is indicated. (b) Relaxed Σ5 CSL. (c) Unrelaxed Σ5 $\frac{1}{\infty}$ (210) state. (d) Relaxed Σ5 $\frac{1}{20}$ (210) state. (e) Relaxed Σ5* CSL. (f) Relaxed Σ5* $\frac{1}{10}$ (210) state.

use of the Starkloff-Joannopoulos *ab initio* local pseudopotential approach.[19] The molecular-dynamics scheme is particularly suited to the relaxing of systems with many degrees of freedom. Briefly, conventional matrix diagonalization is avoided and replaced by simple integration of classical equations of motion for the electrons, ions, and unit-cell volume. This method allows the use of a large number of basis functions and our calculations were performed with an energy cutoff of 10 Ry, which corresponds to about 4300 plane waves. Two Monkhorst-Pack[20] k points were used for Brillouin-zone averaging. No symmetry was imposed on the system and the symmetry-breaking element in the molecular-dynamics method allowed the systems to explore regions of phase space with lower symmetry than the initial configurations.

The results of all our calculations are presented in Table I and Fig. 1. The table lists the total energies for the four twist boundaries considered and the change in grain-boundary volume after relaxation. The geometric structures of the relaxed boundaries are shown in Figs. 1(b), 1(d), 1(e), and 1(f). In the figures, we have arbitrarily chosen to draw bonds between all pairs of atoms that are separated by distances less than 1.15 times the bond length in the bulk. In the extremely distorted environment of the grain boundary, it is possible that atoms separated by this distance could still be bonded although a detailed investigation of the electronic charge density is required to test this. We shall present a detailed study of the bonding in the grain boundaries in a forthcoming publication.

Figure 1(b) shows the structure obtained after allowing the (Σ5 CSL) grain boundary in Fig. 1(a) to relax. The relaxation basically involves the formation of a di-

TABLE I. Grain-boundary energies (E) and local volume changes ($\Delta\Omega$).

Rotation	Translation	Energy (E) (mJ m^{-2})	(eV)	$\Delta\Omega$ (Å)
36.9° (Σ5)	CSL	1288	5.87	+0.07
36.9° (Σ5)	$\frac{1}{20}$ (210)	851	3.88	−0.05
−53.1 (Σ5*)	CSL	1415	6.45	+0.07
−53.1 (Σ5*)	$\frac{1}{10}$ (210)	937	4.27	−0.22

mer bond between a pair of atoms in the layer above the interface. We note that it appears to be energetically *unfavorable* for new bonds to form on *both* sides of the interface. The distortion leaves six atoms per unit cell with only three near neighbors and the structure contains one four-membered ring per unit cell. Fourfold rings of bonds are very unusual in germanium or silicon structures and to our knowledge have never been observed before. They are, however, an intrinsic structural element of this type of twist boundary.

In Figs. 1(c) and 1(d) we show respectively the unrelaxed and relaxed geometries of the $\Sigma 5$ $\frac{1}{20}\langle 210\rangle$ grain boundary. The relaxation in this boundary is much larger than in the previous case and some atoms move distances greater than 40% of the bond length during the relaxation. All the atoms have four near neighbors after distortion and the relaxed structure contains two four-membered rings per unit cell. If the pairs of near-neighbor atoms are assumed to be bonded, all the atoms have fourfold coordination with maximum bond length 13% greater than the bulk value. Unlike the $\Sigma 5$ CSL state, this translation state *does* allow new bonds to form on both sides of the interface.

Figures 1(e) and 1(f) illustrate the geometric structures obtained after the relaxing of two $\Sigma 5^*$ boundaries. Figure 1(e) shows the CSL after relaxation. We find that the distortion has produced three atoms per unit cell which have only three near neighbors and the structure contains four four-membered rings per unit cell. The coincidence-site atom in this structure has five near neighbors as a result of formation of a dimer bond with an atom in the same layer which becomes fourfold coordinated. The occurrence of a fivefold-coordinated atom in this structure is particularly interesting in the context of recent suggestions that such defects may dominate over threefold-coordinated atoms in amorphous silicon.[21] Finally, Fig. 1(f) shows the relaxed $\Sigma 5^*$ $\frac{1}{10}\langle 210\rangle$ state. This boundary relaxes by forming dimer bonds between atoms in the layers above and below the interface. The dimers bond across the interface to form continuous chains of fourfold-coordinated atoms lying along $\langle 310\rangle$ as can be deduced from the figure. However, after reconstruction, there are still two atoms per unit cell that have only three near neighbors and only one weak four-membered ring. We note in particular from Table I that the boundary undergoes a marked contraction in width during relaxation.

For both the $\Sigma 5$ and $\Sigma 5^*$ boundaries, the nonzero-translation states studied had the lowest total energies. It has often been assumed that the presence of the coincidence atom in a site belonging to both crystals would lead to a low-energy boundary. Previous experimental and theoretical results[4,22] for tilt boundaries in semiconductors have shown that this is not necessarily the case and the results of our calculations for twist boundaries in germanium support this. In addition, whereas the CSL states both involve a slight expansion of the local grain-boundary volume, the translated states both undergo a contraction. Previous theoretical studies of grain boundaries in metals and ionic materials have always predicted an expansion at the grain boundary. However, small contractions have been calculated for tilt boundaries in semiconductors with use of simple valence force-field calculations[22] and a possible small contraction in a 22° (001) twist boundary in germanium has been detected experimentally by use of electron diffraction.[5] The magnitude of this contraction is very similar to that reported here.

In any simulated quench or stimulated anneal performed at finite cooling rate there is a possibility that the system will not reach the ground state but will instead remain in a metastable state of higher energy. To test whether our lowest-energy boundary was a metastable state we made a large perturbation to the structure. The perturbation consisted of moving all the atoms in the four layers around the interface by distances of 10% of the bulk bond length. The perturbed configuration was then allowed to relax to equilibrium. Of the twenty ions that were displaced, eighteen moved closer to their positions in the original boundary; but two atoms in the layer immediately below the interface moved further from their original positions in a direction away from the interface, so that the lengths of their bonds across the interface were increased but the bonds to the atoms two layers from the interface were reduced in length. The connectivities of the two relaxed structures were identical and the boundary formed after the perturbation was only 0.1 eV higher in energy than the original boundary. This then leads to a very interesting and unexpected result. The structures with the connectivity of the original boundary lie in an "attractive" region of phase space since the connectivity is not destroyed by a significant perturbation to the system. Moreover, within this region of phase space there are at least two known local energy minima and possibly many more. Tunneling transitions between configurations in the energy minima should then give a range of effects similar to those produced by two-level systems in glasses.[23] Further investigation of the energies of metastable minima and tunneling barriers in this region of phase space is currently underway. Finally, the energy difference between the two local energy minima is smaller than the energy differences between different translation states and this suggests that the $\Sigma 5$ $\frac{1}{20}\langle 210\rangle$ translation state is the lowest-energy boundary of the four studied here. Without calculating the energies of many other translation states, it is not certain that the $\frac{1}{20}\langle 210\rangle$ translation state is the minimum-energy boundary. However, the complete fourfold coordination present in the relaxed structure of this boundary must make it a good candidate.

Finally, we note that the $\Sigma 5$ and $\Sigma 5^*$ grain boundaries are related to one another by the removal or insertion of

an odd number of atomic layers normal to the interface. To fabricate a $\Sigma 5$ boundary experimentally, two oriented crystals with (001) surfaces would be rotated through 36.9° and then sintered together (see, e.g., Ref. 5). In general, the resulting boundary will be a mixture of 36.9° and −53.1° rotations unless the original crystals had monolayer-smooth (001) surfaces. Consequently, a fabricated grain boundary would normally contain *both* $\Sigma 5$ and $\Sigma 5^*$ interfaces.

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[a]Present address: Cavendish Laboratory, Madingley Road, Cambridge, CB3 0HE, United Kingdom.

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THEORETICAL INVESTIGATION OF TWIST BOUNDARIES IN GERMANIUM

M. C. PAYNE*, P. D. BRISTOWE and J. D. JOANNOPOULOS
Massachusetts Institute of Technology, Cambridge, MA 02139, USA
* Present address: Cavendish Laboratory Madingley Road, Cambridge, CB3 OHE, England

ABSTRACT

Results of the first completely ab-initio investigation of the microscopic structure of a grain boundary in a semiconductor are presented. Using the molecular dynamics simulated annealing method for performing total energy calculations within the LDA and pseudopotential approximations, the Σ=5(001) twist boundary in germanium is studied. A low energy structure is identified which exhibits a rigid body translation and a small contraction at the boundary.

INTRODUCTION

Understanding the influence of internal interfaces on the physical properties of semiconducting materials, especially their electrical activity, requires a knowledge of the interfacial structure at the microscopic level. However, the structural complexity of even the simplest interface, such as a homophase grain boundary in an elemental semiconductor, makes this a difficult task both experimentally and theoretically. Experimentally though, new electron diffraction and imaging techniques have begun to yield detailed structural information about a number of grain boundaries in special tilt and twist orientations [1-5]. On the theoretical side, models of semiconductor grain boundaries have generally been limited to simple ball-and-stick constructions [6] and valence force field calculations [7]. Recently, however, first principles approaches to calculating the total energy of solids have been applied to interfaces [8-12]. These studies have provided important information on the distribution of charge density in the boundary, the local density of states, the atomic structure and the boundary energy. However, the methods employed so far have not been entirely ab-initio in the sense that a starting atomic configuration has been assumed based on geometric models or experimental observations and, in the case of the tight binding approach, the potential functions contain experimentally fitted data.

In this paper, we present the first completely ab-initio investigation of the structure of a twist grain boundary in germanium. A method is employed which provides for the self-consistent and simultaneous relaxation of the atomic and electronic configurations. The only input data are the atomic number and mass of germanium.

COMPUTATIONAL METHOD

The calculations were performed using the molecular dynamics simulated annealing method for total energy calculations [13,14]. This method is superior to other total energy calculations in that it allows global minimisation of the energy to be achieved with respect to all electronic and atomic structural degrees of freedom. The contribution to the total energy of the electron-ion interaction is determined using the ab-initio Starkloff-Joannopoulos local pseudopotential for germanium [15]. The exchange-correlation potential is calculated in the LDA of density functional theory using the Perdew and Zunger parameterization [16]. Direct solution of the

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Kohn Sham equations for the valence electron eigenvalues is avoided by integrating the classical equations of motion for the electron states. Similar equations of motion are also integrated for the ionic coordinates and computational cell size. The molecular dynamics method allows the use of a large number of basis states and our calculations were performed using an energy cut off of 10 Ryd which corresponds to ~ 4300 plane waves. Two Monkhorst Pack k points [17] are used for Brillouin zone averaging. A model supercell is used containing twelve (004) diamond cubic atomic layers in which the inner six layers are rotated with respect to the outer six layers to form two identical twist boundaries, the precise geometry of which is described in the next section. Periodic boundary conditions are applied in all directions but no symmetry is imposed on the system and the symmetry breaking element present in the molecular dynamics method allowed regions of phase space to be explored with lower symmetry than the initial configurations. The atoms in the central two layers and the outer two layers are kept fixed in their crystallographic positions but the distance between the inner and outer fixed layers can vary as the local grain boundary volume changes. The atoms in the four layers around each grain boundary are allowed to relax by rapid quenching of their velocities and minimisation is terminated when the forces on the atoms were less than 0.1 eV/Å. Static structures are therefore determined by this procedure although, in general, the method can determine dynamical properties of the boundary.

TWIST BOUNDARY GEOMETRY

We consider the Σ-5(001) twist boundary in the diamond structure, where Σ is the inverse density of coincidence sites. Two distinct Σ-5 boundary structures with the same coincidence site lattice CSL can be formed by rotating one diamond crystal with respect to another about [001] by 36.9° or its complementary angle -53.1° [18]. Both structural variants of the boundary are studied in the present work and are labelled Σ-5 and Σ-5*, respectively. Four CSL unit cells of the unrelaxed Σ-5 boundary are shown in Fig. 1(a) and four cells of the relaxed Σ-5* boundary are shown in Fig. 1(e). The Σ-5 and Σ-5* boundaries are clearly related to one another by a 90° rotation of the diamond crystals or, equivalently, by the removal (or insertion) of an (004) layer adjacent to either boundary followed by a translation of 1/20<315>. Both structures have maximal symmetry for this orientation relationship as discussed elsewhere [19]. The DSC translation vectors which, by definition, conserve the CSL are the same for both boundaries and are 1/10<310> in the boundary plane. Arbitrary in-plane translations do not conserve the CSL structure but two special translations of 1/10<210> and 1/20<310> do produce structures of relatively high symmetry [19]. These translated structures are distinct for Σ-5 and Σ-5* so that, including the two CSL configurations, a total of six geometries exist which have high symmetry. In the pair potential simulation of f.c.c. twist boundaries in metals, such states appear to have the lowest energies [20]. Whether this is true for semiconductors is certainly not clear. Nevertheless, for simplicity, in the present work we have considered the relaxation of three of these geometries (Σ-5 CSL, Σ-5* CSL, Σ-5* 1/10<210>) plus a fourth Σ-5 geometry involving the less special translation of 1/20<210>.

RESULTS

The energies of the four twist boundaries and the change in grain boundary volume after relaxation are given in Table I. The structures of the relaxed boundaries are shown in Figs. 1(b,d,e,f). In the figures, we have arbitrarily chosen to draw bonds between all pairs of atoms that are separated by distances less than 1.15 times the bondlength in the bulk. In the extremely distorted environment of the grain boundary it is possible that atoms separated by this

Table I. Grain Boundary Energies and Local Volume Changes

Rotation	Translation	Figure	Energy mJm^{-2}(eV/unit cell)	Vol Change/ Unit Area,Å
36.9°(Σ-5)	CSL	1(b)	1288 (5.87)	+0.07
36.9°(Σ-5)	1/20<210>	1(d)	851 (3.88)	-0.05
-53.1°(Σ-5*)	CSL	1(e)	1415 (6.45)	+0.07
-53.1°(Σ-5*)	1/10<210>	1(f)	937 (4.27)	-0.22

distance could still be bonded although a detailed investigation of the electronic charge density is required to test this.

Figure 1(b) shows the relaxed Σ-5 CSL structure. The relaxation basically involves the formation of a dimer bond, shown shaded, between a pair of atoms in the layer above the interface. The reconstruction leaves six atoms per unit cell with only three near neighbors and the structure contains one 4-membered ring per unit cell.

Fig. 1(d) shows the relaxed Σ-5 1/20<210> structure. The relaxation in this boundary is much larger than in the previous case and some atoms move distances greater than 40% of the bondlength during the relaxation. New bonds that form are shown shaded. All the atoms have four near neighbors after reconstruction and the relaxed structure contains two 4-membered rings per unit cell. If the pairs of near neighbor atoms are assumed to be bonded, all the atoms have four-fold coordination with maximum bondlength 13% greater than the bulk value. Fig. 1(e) shows the Σ-5* CSL after relaxation. It is seen that reconstruction has produced three atoms per unit cell which have only three near neighbors and the structure contains four 4-membered rings per unit cell which are shown shaded. The coincidence site atom in this structure has five near neighbors due to formation of a dimer bond with an atom in the same layer which becomes four-fold coordinated. Finally, Fig. 1(f) shows the relaxed Σ-5* 1/10<210> state. This boundary relaxes by forming dimer bonds between atoms in the layers above and below the interface. The dimers bond across the interface to form continuous chains of four-fold coordinated atoms lying along <310> as seen in the figure. However, after reconstruction, there are still four atoms per unit cell that have only three near neighbors although the structure does not contain any 4-membered rings. The boundary undergoes a marked contraction in width during relaxation.

For both Σ-5 and Σ-5* boundaries, the translation states studied had the lowest energies. In addition, these states both undergo a small contraction in volume during relaxation. Similar modes of relaxation have been observed in other grain boundaries in germanium, both experimentally [4] and using simple valence force field calculations [7]. Of particular note is the detection of a possible small contraction in a 22° (001) twist boundary in germanium using electron diffraction [5]. The magnitude of this contraction is very similar to that reported here.

The geometrical structure factor F of each of the four boundaries has also been calculated in order to predict the relative intensities of any extra grain boundary reflections present in diffraction space. Following a previous study [21], the structure factor calculation is limited to an H,K,0 reciprocal lattice section, where H and K are orthogonal axes parallel to the reciprocal coincidence site lattice in the boundary plane. A map of $|F(HK0)|^2$ will therefore give a distribution of scattered intensity characteristic of the displacement field parallel to the twist boundary. Figs. 2(a) and 2(b) illustrate the calculated square of the structure factor for the two lowest energy boundaries: Σ-5 1/20<210> and Σ-5* 1/10<210>, respectively. The filled circles indicate the positions of the lattice reflections, projected onto the

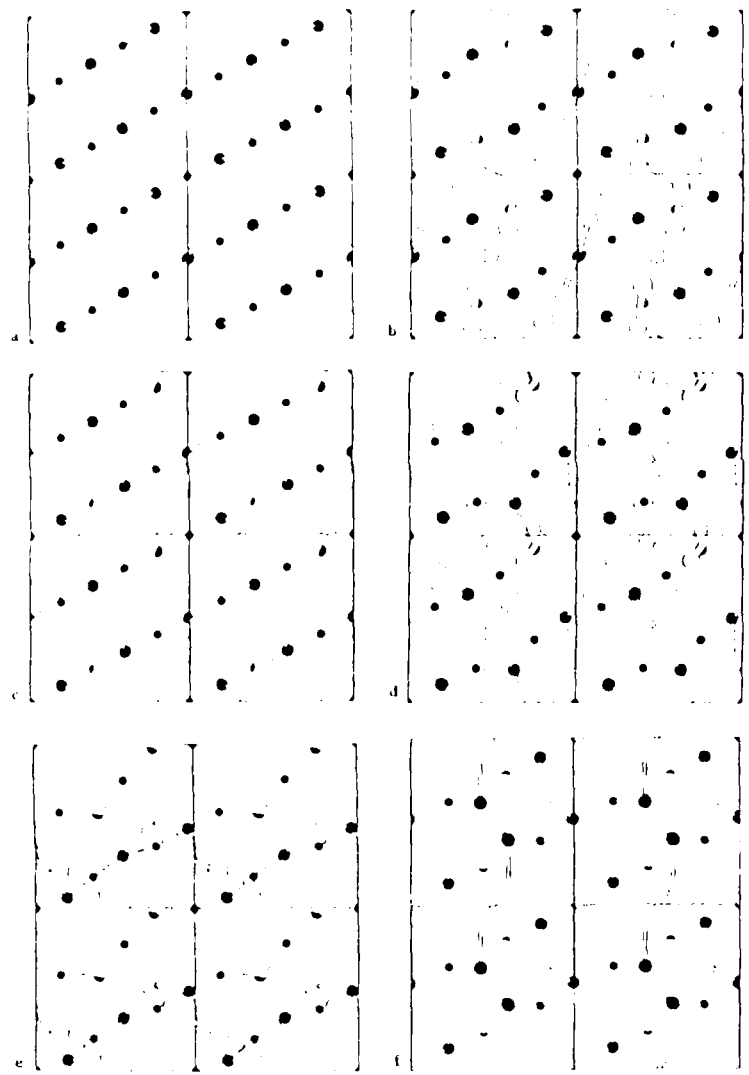

Fig. 1. Atomic positions in the two (004) planes either side of a twist boundary in germanium. Filled and open circles represent atoms in lower and upper crystal, respectively. Four CSL unit cells are shown in each case. (a) unrelaxed Σ=5 CSL, (b) relaxed Σ=5 CSL, (c) unrelaxed Σ=5 1/20·210> state, (d) relaxed Σ=5 1/20<210> state, (e) relaxed Σ=5* CSL, (f) relaxed Σ=5* 1/10·210> state.

HKO plane, and the numbers show the calculated values of $|F(HKO)|^2$ per unit CSL cell. The circled numbers indicate the strongest reflections that might be observed in a diffraction experiment. Since the two distributions of strongest reflections are quite different, the two structures should be distinguishable experimentally. However, it is possible that domains of Σ=5 and Σ=5* structure can coexist in the same boundary separated by partial grain boundary dislocations [18]. The resulting diffraction pattern might therefore be an average of the two patterns calculated here.

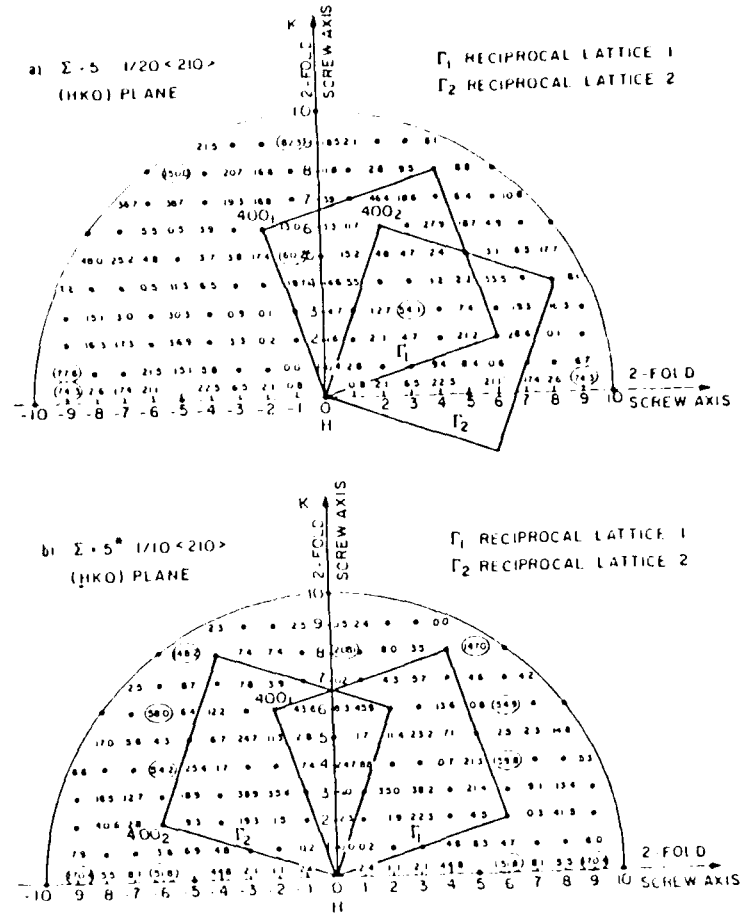

Fig. 2. Calculated values of $|F|^2$ in the HKO reciprocal lattice plane. (a) Σ=5 1/20·210> state, (b) Σ=5* 1/10<210> state. The unit cells of the two rotated reciprocal lattices are shown and the filled circles represent all projected lattice reflections.

DISCUSSION

A completely ab-initio investigation of four twist grain boundaries in germanium has shown that the lowest energy boundaries are translations from the coincidence site lattices and that they exhibit small local contractions compared to that of the perfect crystal. A simple way of rationalising the relative energies of the boundaries is to count the number of intrinsic defects such as 4-membered rings and 3-fold coordinated atoms per unit cell. The lowest energy boundary has two 4-member rings per unit cell but no 3-fold coordinated atoms. Only slightly higher in energy is the boundary that contains no 4-membered rings but four 3-fold coordinated atoms per unit cell. The lowest energy CSL contains six 3-fold coordinated atoms and one 4-membered ring per unit cell while the highest energy structure has three 3-coordinated atoms and four 4-membered rings per unit cell and also contains the defect involving the five-fold coordinated atom. In a simplistic manner, it can be seen that the boundary energies increase as the number of defects increases. An important result also is the determination of a relatively low energy structure that does not have 4-fold coordination. This would indicate that methods which always restrict the coordination to four, such as the valence force field calculations, are erroneously excluding important areas of phase space. We conclude that the molecular dynamics technique proved to be particularly powerful for studying grain boundaries since the method is not sensitive to symmetry and is ideal for studying systems in which large relaxations take place. This provides further motivation for the study of these interfaces using ab-initio methods.

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